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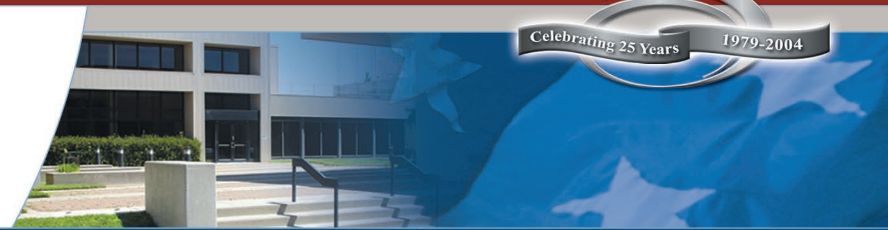
Celebrating 25 Years 1979-2004

CRF NEWS



COMBUSTION RESEARCH FACILITY

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Novel Imaging Technique Opens New Doors for Studying Single Macromolecules and Nanoparticles

CRF researchers have developed a new confocal fluorescence microscope that allows, for the first time, simultaneous measurement of wavelength and emission time with single-molecule sensitivity. This new capability enables entirely new types of temporal and spectral correlation spectroscopy and therefore new insights into the dynamics of single macromolecules and nanoparticles.

The apparatus was developed by Carl Hayden, A. Khai Luong, Claudiu Gradinaru, and David Chandler of the CRF's Chemical Imaging of Macromolecules and Nanosystems group. The group's research interests focus on studies of photophysics of macromolecules in confined and complex environments, including biologically relevant signal transduction and response regulation processes.

Single-Molecule Experiments

Scientists have exploited various fluorescence characteristics, such as intensity, spectrum, lifetime, and polarization, to gain insights into the system under study. By using single-molecule experiments, they can overcome the inherent averaging of observables in ensemble measurements and access photodynamics, such as those involv-

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Sandia National Laboratories

Mass Spectrometry

Sandia Mass Spectrometry Instrument Provides New Capabilities for Probing Complex, Spatiotemporal Reaction Processes

Studying aging in rocket motor propellants and the development of cancerous tumors is difficult because such processes involve complex, nonlinear molecular reactions that frequently occur slowly in localized regions. Yet achieving a better understanding of the underlying fundamental processes is essential, in these examples, to engineering weapon systems that account for age-related degradation and to developing new therapies to fight disease.

A new instrument developed by a team of Sandia researchers can be used to identify the chemical constituents on the surface of a sample as a function of location, providing a chemical map of the compounds comprising the sample. This information will allow the detection of subtle changes in samples and will provide data on their evolution over time.

Located in the CRF, the chemical imaging precision mass analyzer (ChIPMA) was developed by Rich Behrens, Bob Bastasz, Josh Whaley, Sean Maharrey, and Aaron Highley. The instrument is the first in the world to couple a focused ion beam and laser ablation surface analysis system to a high-performance Fourier-transform ion cyclotron resonance (FTICR) mass spectrometer.

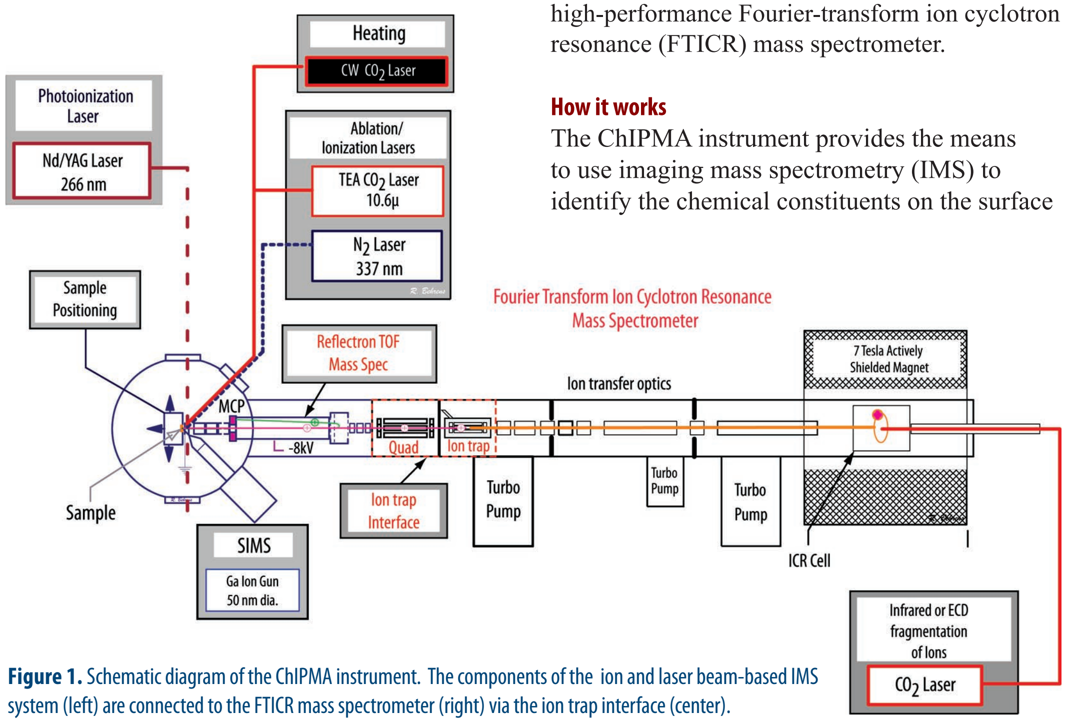

Figure 1. Schematic diagram of the ChIPMA instrument. The components of the ion and laser beam-based IMS system (left) are connected to the FTICR mass spectrometer (right) via the ion trap interface (center).

How it works

The ChIPMA instrument provides the means to use imaging mass spectrometry (IMS) to identify the chemical constituents on the surface of a sample and provides mass spectra of the constituents as a function of position. To implement IMS requires: (1) removing and ionizing representative chemical species from the sample, (2) identifying the chemical species from the mass spectra and their spatial location, and (3) the ability to store and analyze extremely large data sets. The essential features are illustrated in Figure 1.

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Looking Back and Ahead: Perspectives of the Former and New CRF Directors

Bill McLean

Terry Michalske

This year marks the CRF's 25th anniversary and also a change in its leadership. Bill McLean, CRF Director for the past 12 years and Sandia employee for 26 years, retired in early February and is succeeded by Terry Michalske, a longtime Sandia materials scientist and manager (see "New Director Assumes Post at CRF," p. 3). The two recently shared their perspectives on important trends in the CRF's history and the outlook for the coming years.

In his previous position, new CRF Director Terry Michalske was responsible for launching a new Department of Energy Office of Science user facility at Sandia's New Mexico site called the Center for Integrated Nanotechnologies (CINT). In many ways, CINT is patterned after the CRF model in which science is done largely through collaborations among staff scientists and visiting researchers.

"The concept of doing science as a community is really central to the CRF's success. The community of CRF scientists has been highly successfully in focusing on difficult problems, sharing and testing each other's ideas, and collectively advancing energy science and technology. The CRF pioneered this approach, and it will continue to be an inherent part of its future," Michalske said.

While traditional user facilities offer access to equipment and facilities, CRF users can tap into the staff's scientific and technical expertise as well. "The real importance is not of a physical structure but the community of scientists it represents," Michalske said.

> *"Doing science as a community is really central to the CRF's success."*

Former CRF Director Bill McLean agrees that the user facility concept has been essential to the CRF's success. And just as important is the original founders' vision of using state-of-the-art optical methods to probe hostile environments, a pioneering idea that became the CRF's distinguishing characteristic. "This is still what we're doing today with much more understanding and much greater capability. In some ways, laser diagnostic capabilities have advanced analogously to the advances in computing," he said.

Scientists have gone from being able to make point measurements to one, two, and, to some degree, three dimensions in computations and measurements, McLean said. "As we advance in microscale sensor and control devices and use increasingly sophisticated and precise models, we ought to be able to control combustion processes," he said.

A Few Trends

Some other trends that McLean has witnessed since the CRF opened 25 years ago have to do with the makeup of the CRF technical staff and how they work together. The number of postdocs has significantly increased over the years.

"As our reputation grew, we attracted excellent candidates, and we better understood the role of our postdocs in enhancing our productivity," he said. "Of course, another beneficial effect of postdocs is that they promote 'cross fertilization'—dissemination of the CRF's approaches and knowledge—as they move on to positions at universities and in industry."

As experimental data has become more refined and computational capabilities more powerful, McLean has also seen the working relationship grow closer between experimentalists and modelers. Modelers need to validate their work with experimental data, while experimentalists use models to predict results, a trend he predicts that will continue. Both will face the growing challenge of managing all the data generated by increasingly sophisticated techniques and equipment.

Successfully Uniting Basic and Applied Research

The CRF is also a successful model of the integration of basic and applied research, say McLean and Michalske. The Office of Science programs amount to about a third of the CRF's funding, other DOE offices' programs amount to about 40%, and the remainder comes from national security, internally funded R&D, and other miscellaneous sources.

"What I find most impressive about the CRF is that it has attained what is often declared as the objective but seldom achieved, and that's having world-class science connected with and part of an establishment that does real-world technology with impact," Michalske said. "I'm excited to be part of an organization that has those credentials and capabilities, and it's my goal to maintain this vision and strength in the coming years."

Mission Focus Leads to New Opportunities

The CRF's success can also be traced to its efforts to stay focused on its energy mission. "We haven't tried to move toward the 'flavor of the month.' We've kept the mission of solving the nation's energy-related challenges top-of-mind while looking for opportunities to apply new capabilities to other key DOE missions," McLean said.

This has led to many successful collaborations and spinoff technologies—some ongoing or in early stages—including:

- The extension of its strengths in optical diagnostics to remote sensing technologies, such as lidar and remote gas detection
- The development of microscale chemical separation technology for homeland security applications
- The development of instrumentation for use in steel mills, glass production, and studies of fires (used in evaluating the danger by accidents posed to nuclear weapons and critical shipping containers)
- The application of computational techniques to the study of biosystems
- The application of chemical physics and chemical dynamics knowledge and techniques to the development of advanced optical microscopy that allows spectrally and temporally resolved measurements of single molecules

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CRF Director
Terry Michalske

New Director Assumes Post at CRF

Terry Michalske, founding director of the Center for Integrated Nanotechnologies (CINT) at Sandia and Los Alamos national laboratories, became the new director of the CRF on Feb. 4. He replaces Bill McLean, who retired after 12 years as CRF director.

Since 2001, Michalske has been Director of Sandia's Integrated Nanotechnologies Department in Albuquerque, N.M. In that position, he oversaw planning and construction of the Center for Integrated Nanotechnologies (CINT), a $75 million facility dedicated to nanoscience integration that broke ground last spring. CINT is Sandia's second Office of Science user facility, the CRF being the first.

As CRF Director, Michalske will oversee the Biological and Energy Sciences Center, which contains the CRF. Some of Sandia's growing bioscience activities will be folded into the newly reconfigured center with the goal of advancing these efforts at a more aggressive pace.

"This new organization has the opportunity to bring together our strong capabilities in energy science as we build a new bioscience capability at the laboratory," Michalske said.

Michalske joined Sandia in 1981 and has been a manager since 1987, overseeing the Surface and Interface Sciences Department and Biomolecular Materials and Interfaces Department. He has a Ph.D. in ceramic science from Alfred University. His work on stress corrosion fracture of silica has been recognized with several international awards, including the Ross Coffin Purdy Award and the Weyl International Glass Science Award. He is a corecipient of an R&D 100 Award for development of the interfacial force microscope.

DOE Awards Supercomputer Time to CRF Scientists

The Department of Energy (DOE) has awarded supercomputer time at the National Energy Research Scientific Computing (NERSC) Center in Berkeley, Calif., to two CRF scientists to study problems aimed at increasing understanding of ways to reduce pollutants and gain efficiency in combustion devices.

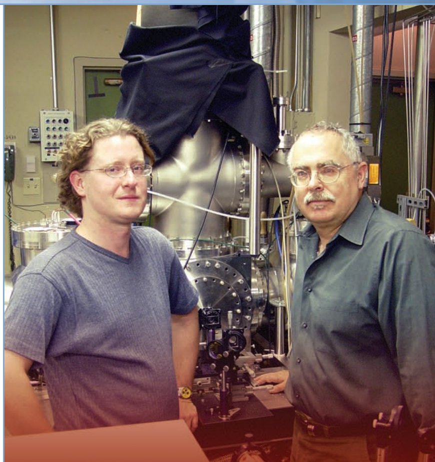
Jacqueline Chen and postdoc Evatt Hawkes received 2.5 million processor-hours through the DOE's Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program, which each year provides computational support for a small number of computationally intensive, large-scale research projects with potential for leading to high-impact scientific advances.

Scaling problems to run on more processors is not only faster but allows scientists to study more complex problems. For example, a calculation run for 2 million hours on a single-processor PC would take 228 years versus 41 days on NERSC's IBM supercomputer.

Of the three awardees for the 2005 INCITE program, the CRF team received the largest allocation of cpu hours for their proposal, "Direct Numerical Simulation of Turbulent Nonpremixed Combustion: Fundamental Insights Towards Predictive Modeling." Twenty-three proposals were submitted.

"We are thrilled at the unique opportunity that the INCITE award provides us," Chen said. "This vast award will enable us to make significant contributions to the challenging problem of understanding and modeling the interactions of turbulence and finite-rate chemical effects in nonpremixed combustion. Ultimately, our plan is to share the resulting data with the turbulent combustion modeling community at large."

Chen and Hawkes will perform detailed three-dimensional combustion simulations of flames in which fuel and oxygen are not premixed. By better understanding the details of such flames, the researchers hope to gain insight into reducing pollutants and increasing efficiency in combustion devices. This research could have applications in such areas as jet aircraft engines, where fuel and oxidizers are not premixed for safety reasons, and in direct-injection internal combustion engines. These simulations would be the first-ever 3-D direct numerical simulations with detailed chemistry of a fully developed turbulent, nonpremixed flame.



Postdoc Bradley Parsons (left) has accepted a postdoctoral position with Professor Daniel Neumark at the University of California, Berkeley. For the past several years, he has worked with David Chandler (right) in the CRF's Combustion Chemistry Department on reactive scattering and photochemistry of bromine compounds.

CRF Joins Postdoc Group

The CRF recently joined the National Postdoctoral Association *(www.nationalpostdoc.org)*, an organization dedicated to enhancing the postdoctoral experience and advancing the U.S. research enterprise. Over its 25-year history, the CRF has employed an increasing number of postdocs, who play an integral role in the CRF's research as well as disseminating knowledge from the CRF to other research institutions. The CRF currently employs about 30 postdocs from all over the world. For information on CRF postdoc opportunities, see *http://www.ca.sandia.gov/crf/employment*.

Jerry Lee (right) left the CRF in February to take a position at United Technologies Research Center. He had been working in the CRF's Reacting Flow Research Department with Habib Najm (left) on the development of chemical model analysis and reduction tools using computational singular perturbation analysis, as well as the coupling of these tools with adaptive tabulation techniques for accelerated adaptive chemistry computation of reacting flows.

Two CRF Groups Receive Best Paper Awards

The Society of Automotive Engineers (SAE) has presented two CRF research groups with best paper awards to be presented at the SAE 2005 World Congress in April.

The Arch T. Colwell Merit Award goes to Chuck Mueller, Lyle Pickett, Glen Martin, and Dennis Siebers from Sandia, and Bill Pitz and Charlie Westbrook from Lawrence Livermore National Laboratory, for "Effects of Oxygenates on Soot Processes in DI Diesel Engines: Experiments and Numerical Simulations." The award, which recognizes authors of papers of outstanding professional or technical merit, is given to less than 1% of SAE papers annually, which totaled about 2,500 for 2003.

The Russell S. Springer Award goes to Lyle Pickett for "Fuel Effects on Soot Processes of Fuel Jets at DI Diesel Conditions," coauthored with Dennis Siebers. The award is given annually to the lead author of an original and outstanding technical paper by a younger SAE member.

Sandia's Mark Zimmerman integrates a hydride bed with temperature monitoring sensors.

Sandia, General Motors Launch Hydride Storage Tanks R&D Effort

General Motors Corp. and Sandia have launched a 4-year, $10 million program to develop and test tanks that store hydrogen in a complex metal hydride. The goal is to develop a pre-prototype, solid-state hydrogen storage tank that will store more hydrogen onboard an automobile than current technologies. The storage design is focused on a sodium aluminum hydride material, but researchers expect the design to accommodate improved hydride storage materials as they become available. GM and Sandia say the program is part of an effort to find a way to store enough hydrogen onboard a fuel cell vehicle to equal the driving range obtained from a tank of gasoline, which will be key to customer acceptance of fuel cell vehicles.

Looking Back (Continued from page 2)

- The extension of state-of-the-art laser technologies to the exploration of high-power fiber laser technologies with a broad array of applications beyond combustion

Although spinoffs will no doubt continue, McLean and Michalske agree that the CRF's work will remain largely focused on energy-related challenges. While the 1970s energy crisis that led to the CRF's formation is history, the nation and the world now face a new kind of crisis: rapid growth in energy demand by developing nations together with the need to better control pollutants and carbon dioxide emissions because of their adverse impact on health and climate, McLean said.

Michalske said that the CRF's leadership role in applying world-leading optical diagnostics and state-of-the-art modeling and simulation toward the study of highly complex systems can help advance our understanding of other complex problems, such as biological systems.

"While the focus on energy must remain a clear objective for the CRF, there are synergies with the capabilities it has developed that create some important opportunities to impact biological and life sciences. We plan to explore bioscience opportunities at the CRF that will support Sandia's missions in energy as well as national security," he said.

Novel Imaging *(Continued from page 1)*

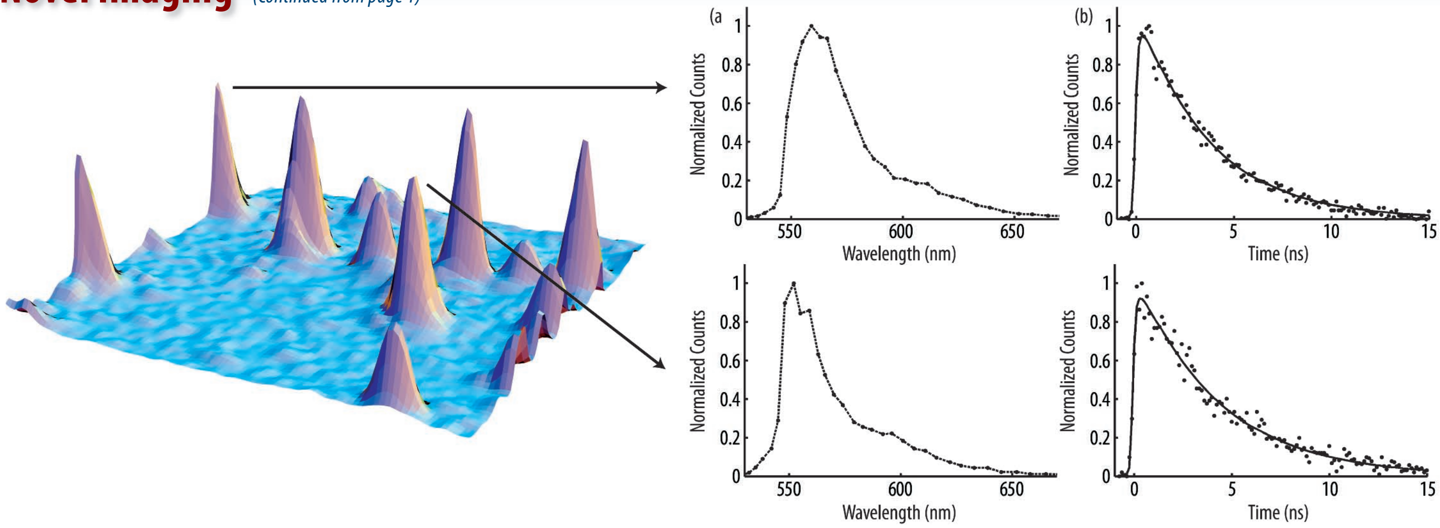


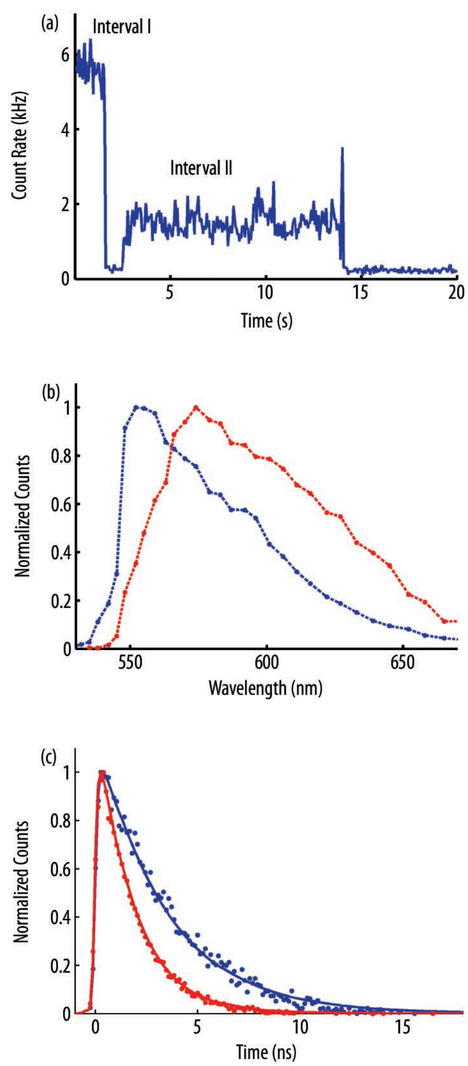
Figure 1. 5 x 5-µm region of a mixed sample of R6G and TMR embedded in a thin layer of PMMA. Column (a) shows the fluorescence spectra and column (b) show the fluorescence lifetimes of the selected peaks. Solid lines in the lifetime plots are the mono-exponential fits to the experimental data. Peak 1 lifetime $\tau_1 = 3.58$ ns, and peak wavelength = 559 nm. Peak 2 lifetime $\tau_2 = 4.14$ ns, and peak wavelength = 552 nm.

ing transient states or energy transfer, and molecular or host dynamics that affect fluorescence characteristics. With the newly developed apparatus, Hayden and his colleagues can further characterize a single-molecule system to gain new insights about the molecule itself and its environment by simultaneously probing multiple parameters of the fluorescent sample.

Unique Capabilities

Figure 1 shows a 3-D fluorescence intensity plot of a 5 x 5-µm region of a sample of mixed rhodamine 6-G (R6G) and tetramethylrhodamine (TMR) dyes embedded in a thin film of polymethylmethacrylate (PMMA). Each peak represents a single molecule in the film. By first establishing the fluorescence characteristics of individual R6G and TMR molecules in PMMA, CRF researchers can use the information to identify the peaks in the 3-D image. In this example, the top spectra result from a TMR molecule, while the bottom spectra are from an R6G molecule.

A powerful and differentiating capability of this new technique is to simultaneously measure the color and time of emission as a function of acquisition time for each detected photon. Figure 2a shows an example of such a time trace for a sample of single Cy3 molecules, a widely used fluorophore for labeling biomolecules, in a PMMA film. The observed intensity changes are indicative that the time trace was taken of a single Cy3 molecule embedded in PMMA. This is supported in particular by the drop in intensity level to background at the early portion of the time trace, where the signal remains for nearly one second before increasing in a single step to above-background levels. It is highly improbable that more than one molecule stops emitting fluorescence photons simultaneously at the end of Interval I and remains synchronously off for nearly a second.



The fluorescence emission spectra and decay curves for the two time intervals are shown in Figure 2b-c, respectively. Correlated with the large fluorescence intensity change, the spectra and lifetimes of the single Cy3 in PMMA also shifted significantly during the time trace. The correlation of the red shift in the broad emission spectrum with a shift to faster fluorescence decays is possibly due to a change in the interaction of the Cy3 with its host site, resulting in faster nonradiative relaxation of the dye molecule.

These examples show that the new confocal fluorescence microscope can be used to identify multiple fluorophore species even when they show minimal differences in fluorescence characteristics. The scientifically more compelling application for this apparatus, however, is to use it to study the fundamental dynamics underlying the photophysics of single molecules, such as changes in internal states of a single molecule, quenching, and resonance energy transfer processes.

Figure 2. (a) Time trace of a diffraction limited spot in a sample of dilute Cy3 embedded in a thin layer of PMMA film. (b) Normalized fluorescence spectra of the time Intervals I and II are shown in blue and red curves, respectively. (c) The corresponding lifetime decays for the two time intervals are shown to fit to mono-exponential curves: the blue curve for time Interval I and red curve for time Interval II.

Mass Spectrometry *(Continued from page 1)*

Specific regions on a sample surface are probed using either liquid metal ion beams (secondary ion mass spectrometry, SIMS) or laser beams (either direct laser ablation or matrix-assisted desorption and ionization, MALDI). The mass spectra are measured either directly with a reflectron time-of-flight (ToF) or indirectly by accumulating ions in an ion trap and then transporting them to an FTICR mass spectrometer. The high mass resolution (m/Δm ~200,000) and high mass accuracy (<1 ppm) of the FTICR mass spectrometer, along with its ability to conduct multistage mass spectrometry/mass spectrometry ion fragmentation experiments, provides the ability to identify complex chemical constituents.

Testing

Initial tests with the instrument have focused on developing SIMS methods to probe polymers and LIGA manufacturing processes. (LIGA is a micromachining technology whose name derives from the German words for lithography, electroplating, and molding.) Figure 2 shows the FTICR SIMS spectra of polystyrene deposited on a silver substrate. The broad spectrum shows the distribution of oligomers in the polystyrene sample. The inset shows the expanded spectrum of the n = 18 polystyrene oligomer/Ag+ complex and illustrates the high resolution and high mass accuracy aspects of the system.

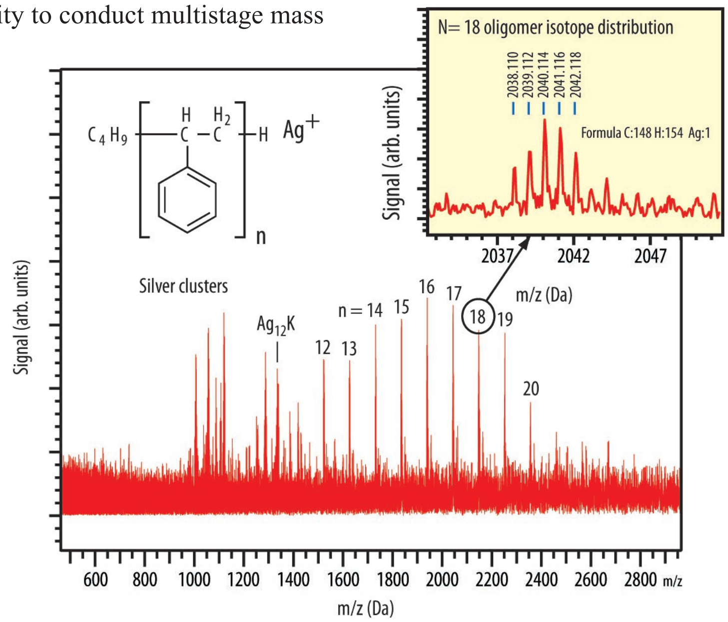


Figure 2. FTICR SIMS spectrum of polystyrene on a Ag surface. Ions were desorbed with a 25 keV Ga^+ liquid-metal ion gun. Inset shows expanded mass region of the n = 18 polystyrene oligomer/Ag complex and illustrates the isotopic distribution of the $C_{148}H_{154}Ag$ ion.

We tested the IMS aspects of the instrument with a spring manufactured by a LIGA electrochemical deposition process. An alloy of 99%Ni/1%Mn is deposited in a LIGA mold. We used SIMS-IMS measurements to determine whether the Ni and Mn were uniformly deposited and whether the alloy contained other contaminants. The principal components in the spatially dependent SIMS spectra were determined using the Automated eXpert Spectrum Image Analysis (AXSIA) algorithms developed by Paul Kotula and Mike Keenan of Sandia. AXSIA is a multivariate statistical analysis tool kit developed at Sandia that looks for trends in complete data sets.

We have demonstrated the fundamental operation of the ChIPMA instrument. Future work will focus on developing specific analysis methods to examine reaction details of both manmade and natural systems.

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